Characteristics of Thin Gold-Manganese Films

By

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CHARACTERISTICS OF THIN GOLD-MANGANESE FILMS

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TABLE OF CONTENTS

	Page No.
Introduction	1
Preparation of Alloys	3
Preparation of Film	5
Equipment and Measurements	8
Data Obtained from Films	9
Tables of Data	11
Conductance and Transmission Curves	17
Efficiency Curve	18
Spectral Curves	19
Electron Microscope Photographs	20
Results and Conclusions	23
Vita	26
Bibliography	27

INTRODUCTION

The work described herein is concerned with the condensation characteristics of thin metal films. Gold, manganese, and gold-manganese alloys were used. It has been noted (7,9,10) that in very thin films gold is in the form of discrete particles. It is believed that this is due to atomic migrations of less than five hundred Angstrom units when the gold is deposited from molecular rays. (3,5) This would destroy the possibility of conductivity in such thin films. Dr. E. J. Serfass suggested (8) that if small amounts of manganese are alloyed with gold this basic difficulty might be overcome and a continuous layer formed. A continuous layer would display low resistivity and an electron microscope pattern quite dissimilar to that of pure gold. These characteristics and transmission in the infra red, visible, and ultra violet spectra were studied.

During World War II there was some success in perfecting electrically conducting, transparent materials. The process developed involved the use of thin metal or metal oxide films applied by spraying. The metal usually used was tin.(1,2) These films are generally over one thousand Angstrom units in thickness. The substrata are often optically distorted due to the heat necessary during application and many oddly shaped objects cannot be plated easily by present methods.

Thin metal films of gold or a gold alloy less than fifty Angstrom units in thickness, should provide the desired characteristics of

transparency and resistivity, if the basic difficulty is overcome. Useful applications for the Naval Establishments include non-icing and non-fogging windows and transparent shielding for high frequency radiation.

PREPARATION OF ALLOYS

Gold can be made to alloy with almost all other metals, however most of these alloys are of little importance. (6) Gold alloyed with 0% to 40% manganese forms a solid solution with a melting point minimum of 977° C at 12% manganese. The alloys up to 22% manganese can be homogenized. (4)

Four alloys were made containing 2½%, 5%, 10%, and 20% manganese. In preparing these alloys 325 mesh fine gold powder and fine manganese powder were used. The crucible used in preparing the melts consisted of a one-half inch graphite rod hollowed and lined with magnesium oxide. The rod was then baked into a one inch layer of aluminum oxide. The crucible containing the powders, thoroughly mixed, was placed under a helium atmosphere within an induction coil of a Lepel high frequency converter and melting occurred when the eddy currents generated in the graphite had heated it sufficiently. Each sample consisted of approximately 2 grams of powder and upon cooling the melts were small buttonlike pieces.

All samples were then homogenized at approximately 1100° C for six hours under normal atmosphere. During this period a film of manganese oxide formed on the samples and was removed by washing in hydrochloric acid.

The 2½% and 5% alloys were then rolled into foil from which pieces of the desired weight could be cut. The 10% and 20% alloys

were extremely brittle and were broken into smaller pieces which were filed down to the weight desired and into a useable shape.

PREPARATION OF THE FILMS

The films were made by vacuum evaporation of definite amounts of alloy from a tungsten filament. The tungsten filament was located 10 inches, 14.1 inches, 17.3 inches, and 20 inches above four glass plated upon which various substrata were placed for plating.

The thickness of the films was determined in the following manner:

> It was assumed the sample evaporated from a point source and equally in all directions. Thus a known amount of material is evaporated from the center of an assumed sphere of known radius. The thickness of the film formed on the inner surface of the sphere, or in this case on the substrata, can thence be calculated. Using the various distances mentioned above and assuming .1 gram of material, evaporated films of the following thicknesses, in Angstrom units, would be obtained:
>
> 10 inches - 64
> 14.1 inches - 32
> 17.3 inches - 21
> 20 inches - 16

Five types of substrata were used, namely: soft glass, a polyester plastic (mylar), a methacrylate plastic, sodium chloride crystals, and 99.9% silica (vicor).

A pure gold sample and a pure manganese sample were evaporated first. For these runs, in addition to the above mentioned substrata, electron microscope grating specimens were also included. These were used in the electron microscope to determine the nature of the films.

When it was determined that the alloy films varied from the gold,

similar electron microscope specimens were included in a second run of the 5% alloy and their character determined.

Prior to plating, the glass and visor were soaked in sulfuric acid saturated with chromic acid and then washed in water and placed in isopropyl alcohol vapor. When dry the ends of the one inch glass slides were painted with an air drying silver paint. The plastic samples, also one inch in width, were thoroughly wiped with cotton cloth and then silver paint stripes put on them one inch apart. The sodium chloride crystals were prepared using 100% ethyl alcohol and flannel.

For evaporation the pure gold sample was in the form of number thirty wire and short segments were hung from adjacent loops of the tungsten filament. However, great difficulty was encountered with the alloys in foil form. The manganese had imparted a slight brittleness to the alloy and any sharp bend became a minute crack in the small pieces of foil. Thus if the small, single layer pieces were hung from the tungsten loops upon heating the filament vapor pressure lifted the very light foil from the filament. If several layers of foil were folded into a small strip numerous small cracks appeared, especially where the strip was hung from the filament, and when the filament was heated melting occurred near this flaw first and the sample dropped off in two pieces. Numerous variations were tried using an open wound filament without success. The method finally used consisted of turning a filament one quarter inch in diameter with the loops 1/64 to 1/32 of an inch apart. A small roll of alloy foil was then inserted into the filament.

Upon heating the alloy melted into droplets on one or two loops and there was no loss. The small pieces from the 10% and 20% alloys were also used in this closely wound helix. The manganese sample was prepared in a manner similar to the 10% and 20% alloys and also evaporated from the same helix.

EQUIPMENT AND MEASUREMENTS

Resistance measurements of the glass and plastic samples were taken on a General Radio precision impedance bridge. The readings from the plastic samples gave resistance in ohms per unit area directly; the readings from the glass samples were divided by the length of the slide to give the resistance in ohms per unit area.

Infra-red spectra were obtained from the films on the sodium chloride crystals using a Perkin-Elmer automatic recording infra-red spectrophotometer in the two to ten micron range.

The vicor samples provided visible and ultra violet spectra from 2200 Angstrom units to 7500 Angstrom units on a Warren Electronics automatic recording Spectracord.

Adhesion of the films to the glass samples was noted in two ways. Firstly, a one inch strip of scotch tape was firmly affixed to the glass and then peeled off. Any change in the film was noted. Secondly, each glass slide was wiped with a cotton rag and any effect on the film was noted.

The electron microscope specimens were examined in an RCA electron microscope type emu.

DATA OBTAINED FROM FILMS

The results obtained from both metals and each type of alloy are tabulated on the following pages. The scotch tape test for adhesion did not impair the film on any samples, therefore, only the wipe test for adhesion is tabulated.

Figure 1 illustrates the variance in conductivity and transparency with the addition of manganese to gold. Figure 2 shows the efficiency of the films, based upon an index combining transmission and resistance, against the percentage of manganese.

This index was computed assuming optimal desired transmission and resistance are 100% and 150 ohms per unit area respectively. These conditions were assigned an index of 10. Resistances between 100 and 300 ohms per unit area were assigned the number 10; resistances of 50 to 100 ohms and 300 to 1000 ohms per unit area were assigned the number 5; resistances 0 to 50 ohms and above 1000 ohms per unit area were assigned the number 3, with the exception that infinite resistance was assigned 0. These resistance numbers, determined for the films of approximately 32 Angstrom units in thickness, were multiplied by the per cent transmission at 5000 Angstrom units and the product was the desired index.

Figure 3 shows the ultra-violet, visible and infra-red transmission spectra for the 10% manganese film, 33 Angstrom units in thickness.

Films of approximately 32 Angstrom units in thickness were used for all three figures. At this thickness pure gold films show infinite

resistance and those of the alloys give measureable resistance. In thicker films pure gold shows low resistance, indicating the discrete particles are in contact. Films of lesser thickness in the alloys display high resistance and/or very low transmission.

The electron microscope specimens photographed were those with pure gold, pure manganese, and 5% manganese - 95% gold films. The films are approximately 32 Angstrom units in thickness. The photographs follow Figure III.

TABLE I

PURE GOLD

Film Thickness (Angstrom Units)	Resistance per square (ohms)	Range for Transmission over 60% (Angstrom Units)	Maximum Transmission & Wave Length (Angstrom Units)	Adhesion
128	Glass 10.6 Mylar 6.4 Methac 4.2	none	5150 - 51%	poor
64	Glass 92	none	5150 - 58%	poor
42	Glass 205 Mylar 86 Methac 66	4750 - 5500	5150 - 64%	poor
32	Glass inf Mylar inf Methac inf	4050 - 5600	5150 - 67%	poor

TABLE II

PURE MANGANESE

Film Thickness (Angstrom Units)	Resistance per square (ohms)	Range for Transmission over 60% (Angstrom Units)	Maximum Transmission & Wave Length (Angstrom Units)	Adhesion
129	Glass 330	none	100,000 - 21%	good
64	Glass 522	none	100,000 - 50%	good
42	Glass 1100	above 75,000	100,000 - 63%	good
32	Glass 5500	above 21,000	100,000 - 75%	good

TABLE III

97½% GOLD - 2½% MANGANESE

Film Thickness (Angstrom Units)	Resistance per square (ohms)	Range for Transmission over 60% (Angstrom Units)	Maximum Transmission & Wave Length (Angstrom Units)	Adhesion
68	Glass 35 Mylar 20 Methac 50	4450 - 7500	5250 - 60%	poor
34	Glass 1000 Mylar inf. Methac inf.	2780 - 9000	4950 - 74%	poor
23	all infinite	2590 - no limit	beyond 100,000	poor
17	all infinite	2590 - no limit	beyond 100,000	poor

TABLE IV

95% GOLD - 5% MANGANESE

Film Thickness (Angstrom Units)	Resistance per square (ohms)	Range for Transmission over 60% (Angstrom Units)	Maximum Transmission & Wave Length (Angstrom Units)	Adhesion
97	Glass 20 Mylar 16 Methac 18	none	5150 - 44%	poor
49	Glass 67 Mylar 270 Methac 110	4700 - 6200	5150 - 64%	poor
32	Glass 275 Mylar inf Methac inf	3700 - 6200 & above 20,000	5050 - 72%	poor
24	Glass 21M Mylar inf Methac inf	3100 - 5650 & above 20,000	5050 - 66%	poor

TABLE V

90% GOLD - 10% MANGANESE

Film Thickness (Angstrom Units)	Resistance per square (ohms)	Range for Transmission over 60% (Angstrom Units)	Maximum Transmission & Wave Length (Angstrom Units)	Adhesion
100	Glass 44 Mylar 57 Methac 80	none	5150 - 44%	fair
50	Glass 74 Mylar 170 Methac 255	none	5150 - 55%	poor
33	Glass 200 Mylar 960 Methac 630	4550 - 5300	5150 - 63%	poor
25	Glass 1050 Mylar 320 Methac 41	3000 - 7000	5150 - 70	poor

TABLE VI

80% GOLD - 20% MANGANESE

Film Thickness (Angstrom Units)	Resistance per square (ohms)	Range for Transmission over 60% (Angstrom Units)	Maximum Transmission & Wave Length (Angstrom Units)	Adhesion
124	Glass 32 Mylar 30 Methac 36.5	none	5250 - 19%	good
62	Glass 76 Mylar 77 Methac 67	none	6050 - 38%	good
41	Glass 190 Mylar 174 Methac 186	none	6050 - 52%	poor
32	Glass 265 Mylar 780 Methac 510	6000 - 7000	6050 - 60%	poor

FIGURE I

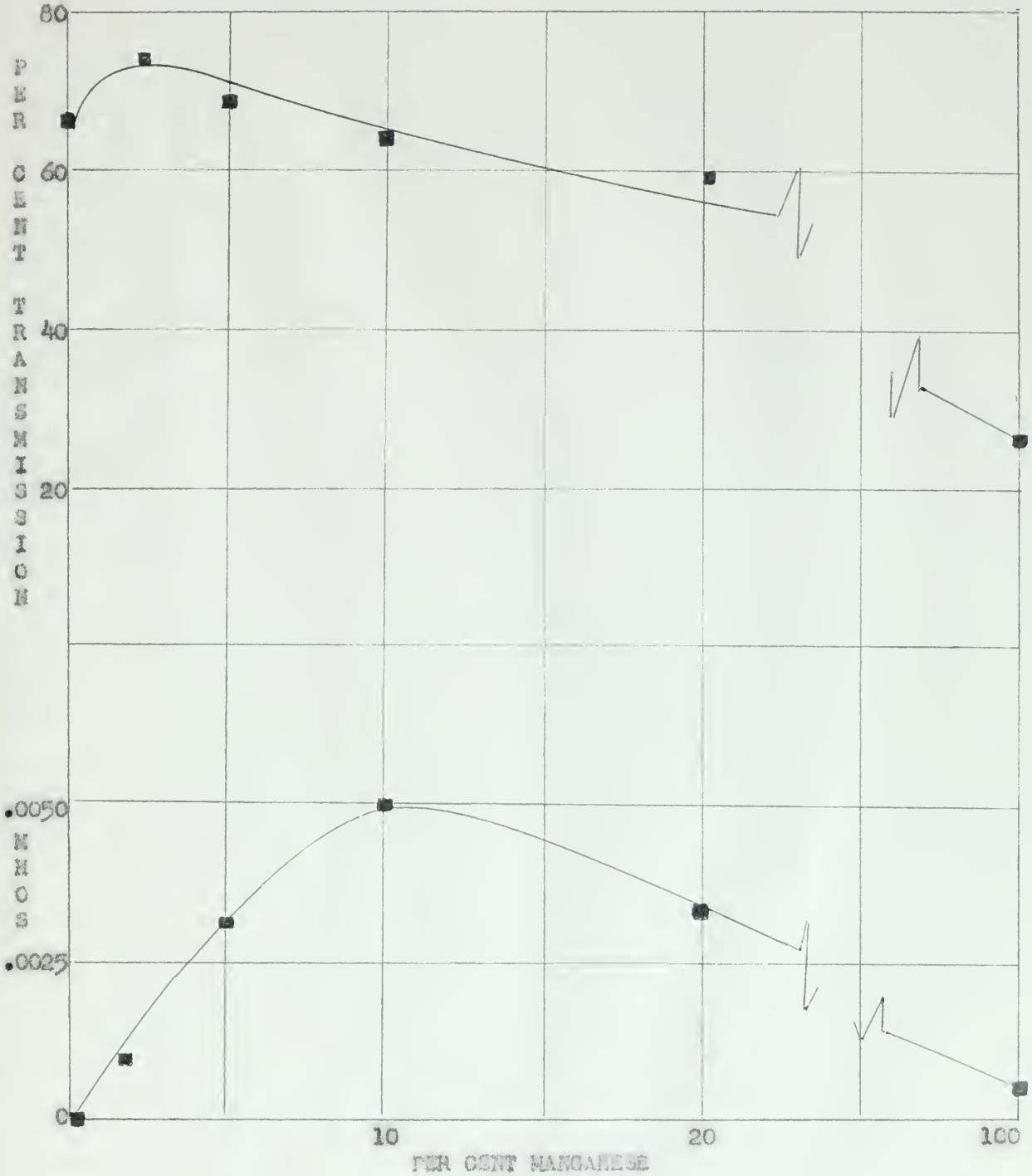

80
60
40
20
PER CENT TRANSMISSION
.0050
MHOS
.0025
0
10
20
100
PER CENT MANGANESE

FIGURE II

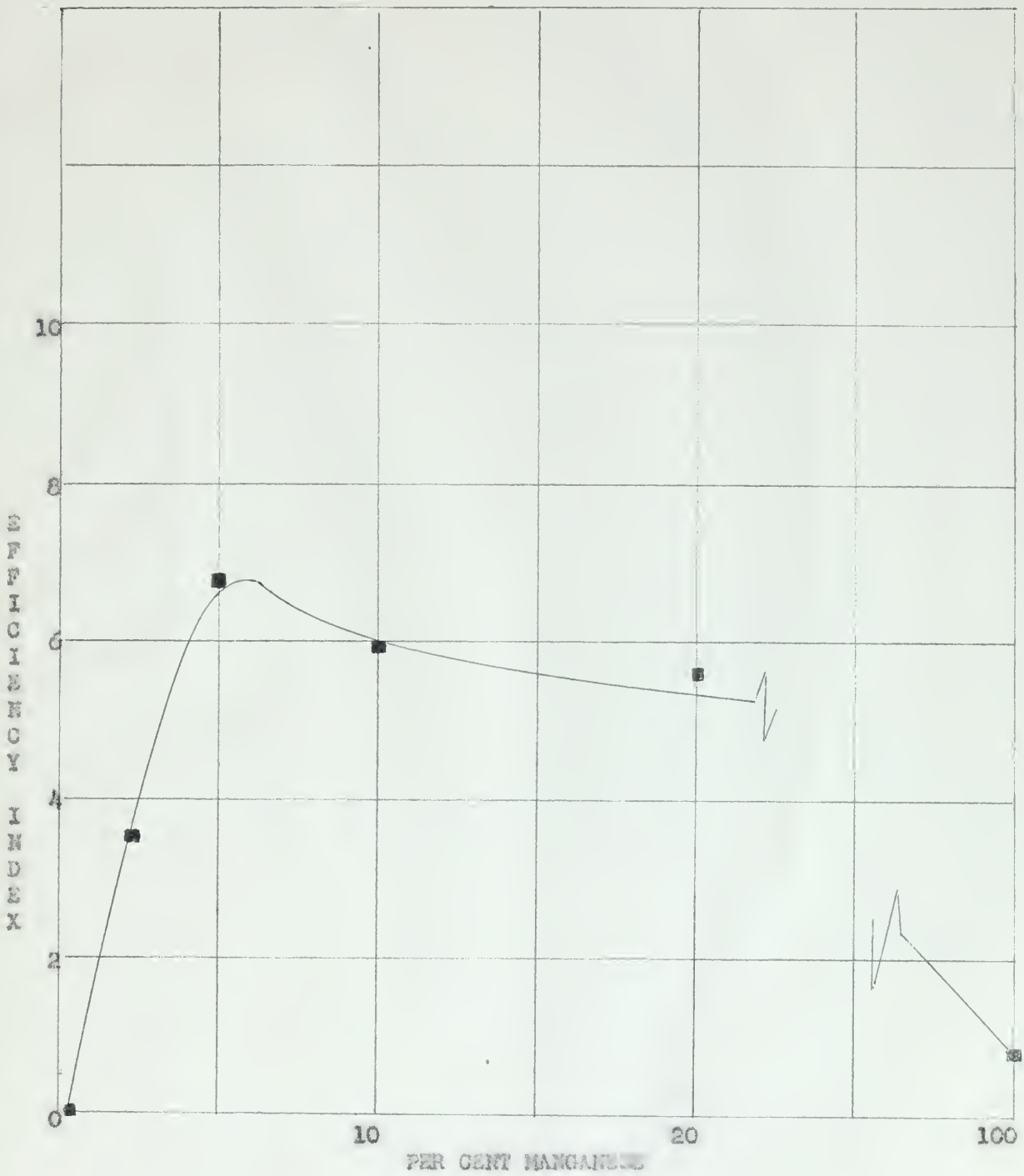
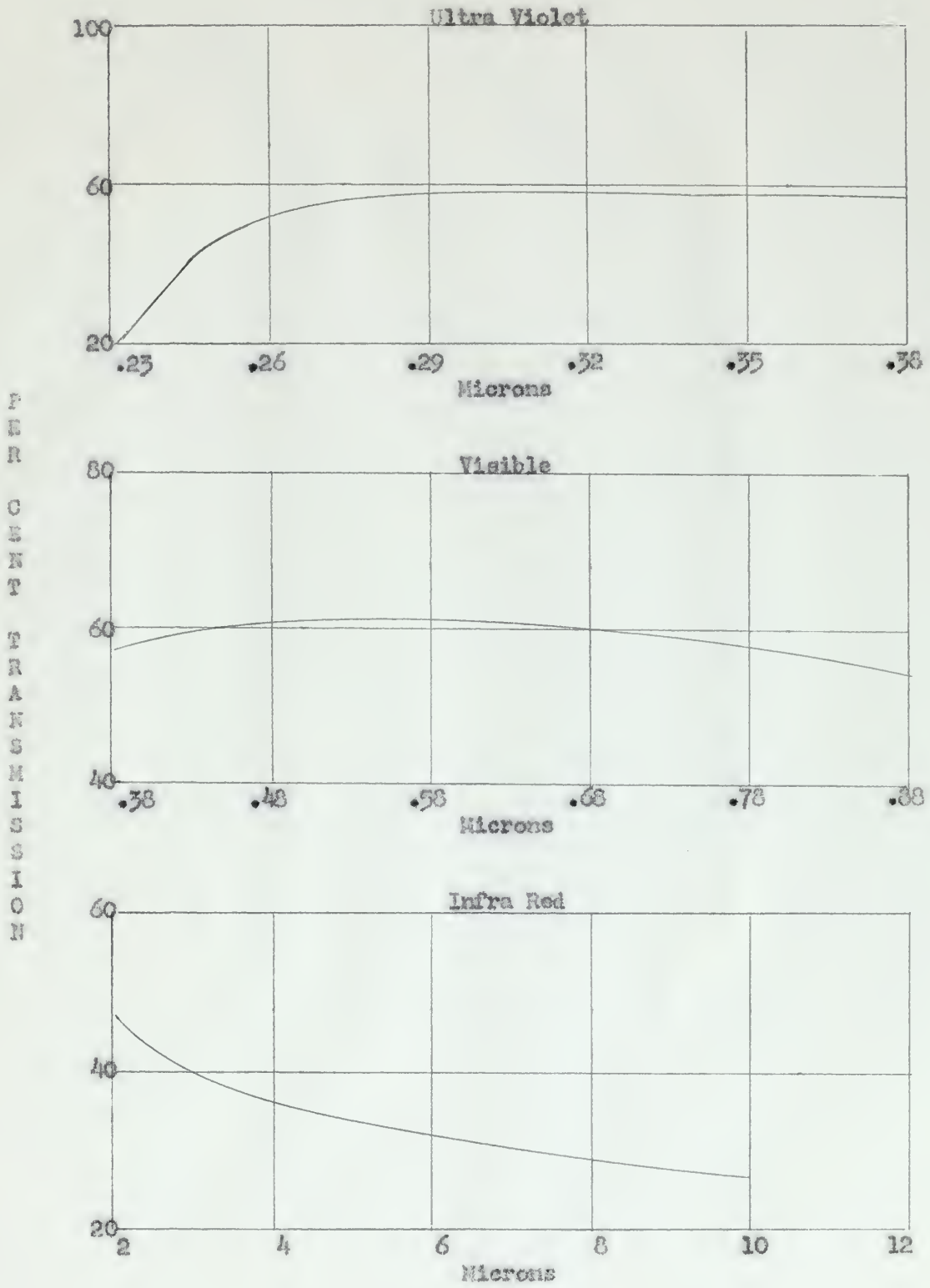
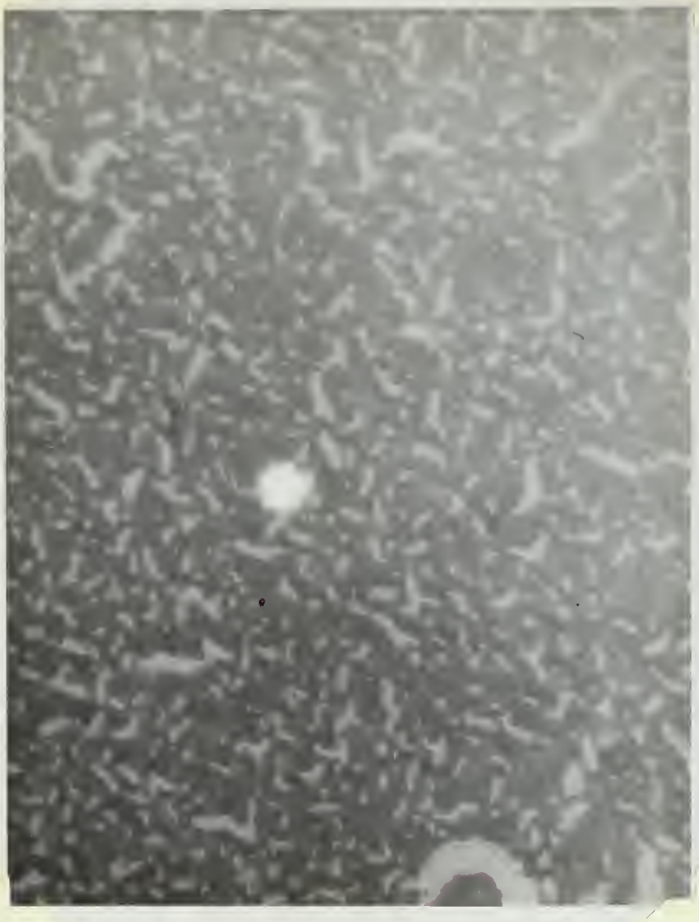


FIGURE III


Ultra Violet
100
60
20
.23
.26
.29
.32
.35
.38
Microns
PER CENT TRANSMISSION
Visible
80
60
40
.38
.48
.58
.68
.78
.88
Microns
Infra Red
60
40
20
2
4
6
8
10
12
Microns

PHOTOGRAPH I



GOLD

PHOTOGRAPH II

5% MANGANESE - 95% GOLD

PHOTOGRAPH III

MANGANESE

CONCLUSIONS AND RECOMMENDATIONS

From the results of this work it does appear that manganese has a decided effect upon the condensation of gold. In films of approximately thirty Angstrom units in thickness gold displays infinite resistance or zero conductance. As is shown in Figure I the addition of manganese causes an increase in conductance to a maximum of .005 mhos per square at about ten per cent manganese. Thereafter, there appears to be a steady decrease until the conductance of pure manganese is reached at .0005 mhos per square.

The curve showing per cent transmission at 5000 Angstroms, of films 32 Angstrom units in thickness, does not have the regularity that might be expected, that is, a steady decrease with the addition of manganese. However, the variance noted between zero and five per cent is not so large that it indicates unusual circumstances.

The electron microscope photographs appear to substantiate the character of the films. Photograph I, pure gold, shows discontinuities which would account for the infinite resistance. The discrete globules must be numerous enough, at this thickness, to partially coalesce but not form a continuous film. Photograph II, 5% manganese - 95% gold, shows a continuous film at approximately the same thickness. Photograph III, pure manganese, shows an extremely even continuous film.

The resistance readings for the two types of plastics are not as complete as those for glass due to the fact that on numerous occasions the heat generated by the filament during the evaporation caused

destruction of the samples. Although some of the readings given from the plastic samples are quite at variance with those of the glass it is felt that this is due to the impossibility of preparing the plastic in the similar thorough manner before plating. As the preponderance of resistance readings seem quite similar it is felt that the films condense on the glass and plastics in a similar manner.

The very definite uptrend in transmittivity of the pure manganese films in the infra red did not seem to be imparted to the gold films. Several films gave a rising transmittivity spectrum in the infra red but it was confined to those of high or infinite resistance and thus could be attributed to holes in the film that allowed infra red to go through unobstructed.

The addition of manganese did not seem to have much apparent effect upon the ultra violet spectra of the various films. The pure gold films and those with 20% manganese were almost superimposeable. In the region from 3600 to 7000 Angstrom units the manganese tended to lower a peak noted in the pure gold films at about 5150 Angstrom units and level off a definite downward trend from the peak to 7000 Angstrom units. With 5% manganese there was noted the unusual circumstance of the 32 Angstrom film giving better transmittivity between 4000 and 6000 Angstrom units than the 24 Angstrom film.

The results obtained from this work are not as useful as had been hoped for. However, if no other alloying element can be found that will overcome the basic difficulty of gold, or other elements of high

conductivity, in the range below 30 Angstrom units, and simultaneously allow transmittivity in the visible region above 70%, it is believed that a comprehensive study of gold-manganese alloys between five and ten per cent manganese and under thirty-five Angstrom units in thickness should provide an alloy and film thickness that can give 70% transmittivity and the required conductance.

VITA

Louis Tuck Renz was born 6 July 1925 at Billings, Montana, the son of Marjorie E. and George W. Renz. Until his entrance into the U. S. Naval Academy, Annapolis, Maryland on 19 July 1943 he lived in various towns in Western Montana and attended several elementary and secondary schools. A B.S. degree was received upon graduation from the Naval Academy 5 June 1946. Seven years of active duty on various ships and stations in the Pacific preceded entry into the U. S. Naval Postgraduate School, Monterey, California on 27 July 1953. On 17 July 1954 LT Renz married Miss Janet Helen Ragsdale at Stanford University Chapel. A second B.S. degree was received from the U. S. Naval Postgraduate School on 3 June 1955. Matriculation at Lehigh University was 18 September 1955.

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